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SOLID PHASE EXTRACTION OF TRIAZINES AND ORGANOPHOSPHOROUS
COMPOUNDS FROM DRINKING WATER.

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The objective of this work was to determine the feasibility of using solid phase extraction (SPE) for the analysis of organophosphorus compounds and triazines present in water. Current methodology involves the liquid liquid extraction (LLE) of the organophosphorous compounds at neutral pH using dichloromethane. A separate LLE using dichloromethane at pH 12 is necessary for the triazines.

The LLE methodology is well established but suffers from the fact that the "wet chemistry" can not easily be automated. It is time consuming, requires extensive labour, and large amounts of expensive and toxic solvents. Our earlier work with the application of SPE to chlorophenols and phenoxyacid herbicides, and, also, to polyaromatic hydrocarbons showed that for these compounds SPE tended to have higher recoveries and lower standard deviations than LLE and led us to believe that SPE might also be applicable to triazines and organophosphorous compounds.

The objective of this research was the development of a simple, rugged method that would be amenable to the eventual introduction of robotics and that would allow the simultaneous analysis of both triazines and organophosphorous compounds in drinking water. In the course of the project, parameters investigated included:

1) The solid phase and eluting solvent. Phenyl, cyclohexyl, octadecyl and cyanopropyl phases and the three eluting solvents, methanol, hexane and ethyl acetate were evaluated. The best combination was the octadecyl phase using ethyl acetate as the eluting solvent. Elution with hexane gave low recoveries with all phases. Elution with either methanol or ethyl acetate gave poor recoveries with both the cyanopropyl and cyclohexyl phases, moderate recoveries with the phenyl phase, and highest recoveries with octadecyl packings.

2) Columns from different manufacturers. Octadecyl columns manufactured by Baker, Supelco, Waters, Analytichem and Alltech were tested using ethyl acetate as the eluting solvent. Under these particular conditions, the columns manufactured by Alltech exhibited lower recoveries than the others but the remaining four were comparable to each other.

3) Consistency of recoveries. The recoveries over a one hundred fold range of analyte concentrations (e.g., from 50 to 5000 ng/L for atrazine and 20 to 2000 ng/L for parathion) were found to be consistent.

4) Different matrices. The recoveries from each of the natural waters; Verner raw water, Lakeview raw water, Ottawa city tap water, and a drilled rural well, and from one reference water (supplied by Dr. Brian Hollebone of Carleton University) were determined at pH 12. The recoveries were high for the triazines but much more variable for the organophosphorous compounds. Later work indicates that much of the variability for the organophosphorous compounds was due to the high pH.

5) Effect of pH. Recoveries were determined at both pH 7 and pH 12. The triazines had high recoveries at both pHs whereas those of the organophosphorous compounds were much greater at pH 7.

6) Effect of Storage. The stability of analytes at two different concentrations adsorbed onto an octadecyl solid phase and stored for times of one day, one week, one, two and three months at room temperature prior to elution were investigated. The adsorbed triazines were stable over this time period whereas the recoveries of the organophosphorous compounds steadily decreased with time. For example, the percentage recoveries of atrazine, alachlor, diazinon and parathion decreased from 105, 112, 101 and 103 following one day of storage to 86, 96, 45 and 36 after three months of storage, respectively.

7) Addition of methanol to the aqueous phase. It has been reported in the literature that the addition of ten percent methanol to the aqueous phase prior to extraction improves the recoveries of the triazines. Under our conditions, recoveries decreased slightly on the addition of methanol.

8) Levels of interferences. When SPE is applied to the analysis of chlorophenols and phenoxyacid herbicides in water using an electron capture detector for quantitation, interferences are significant. Throughout the course of this work (which used a thermionic specific detector) interferences were not a significant problem, although an occasional low level interference with bladex was noted.

9) Real samples. Fortified samples of Ottawa City Tap Water and Rideau River Raw Water at pH 7 were extracted and analyzed the same day. The results appear in Tables 1 and 2.

Table 1: Recoveries (%) of Triazine Herbicides and Organophosphorous Compounds from Ottawa City Tap Water at pH 7 using SPE with an Octadecyl 500 mg Column

Compound	Concentration (ug/L)	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5	Mean	Standard Deviation
Dichlorvos	1.00	103.5	106.3	112.2	126.0	100.0	109.6	9.1
Nevinphos	1.88	116.2	116.0	125.6	143.3	111.0	122.4	11.5
Phorate	0.38	99.2	96.1	108.3	116.4	94.8	103.0	8.2
Atraton	6.25	109.9	98.2	116.5	124.2	91.8	108.1	11.8
Diazinon	1.00	110.4	105.3	117.7	128.8	101.7	112.8	9.7
Propazine	7.50	110.5	100.1	115.3	119.4	95.5	107.8	9.6
Atrazine	6.25	110.9	101.8	114.0	121.4	94.9	108.6	9.3
Siazazine	2.50	111.2	102.6	116.3	125.0	94.2	109.8	10.7
Reidan	1.88	94.8	85.6	98.7	106.2	83.4	93.7	8.4
Bonnel	1.88	79.3	73.8	81.6	91.8	67.8	78.9	8.0
Alachlor	5.00	111.2	100.6	113.8	119.7	93.5	107.8	9.4
Ametryne	4.38	109.3	96.4	111.3	120.2	89.7	105.4	10.9
Sencor	5.00	110.0	98.8	114.7	120.2	92.1	107.2	10.3
Dureban	3.13	70.0	63.1	71.5	82.0	59.4	69.2	7.8
Malathion	1.88	105.8	98.6	118.7	124.6	94.1	108.4	11.6
Parathion	0.38	107.7	99.3	113.1	119.6	91.3	106.2	10.0
Bladex	3.75	108.8	93.1	114.6	118.7	85.9	104.2	12.6
Methyl Trithion	11.25	78.9	68.3	83.4	92.3	63.9	77.3	10.2
Ethion	3.75	60.5	53.3	62.6	75.2	49.4	60.2	8.9

Table 2: Recoveries (%) of Triazine Herbicides and Organophosphorous Compounds from Rideau River Raw Water at pH 7 using SPE with an Octadecyl 500 mg Column

Compound	Concentration (ug/L)	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5	Mean	Standard Deviation
Dichlorvos	1.00	82.4	89.1	87.7	96.7	109.2	93.0	9.3
Nevinphos	1.88	97.3	114.2	103.9	121.2	134.1	114.1	12.9
Phorate	0.38	90.4	101.3	89.0	107.7	112.6	100.2	9.3
Atraton	6.25	112.4	104.4	101.3	107.8	126.2	110.4	8.7
Diazinon	1.00	105.6	115.5	103.0	122.9	127.4	114.9	9.5
Propazine	7.50	108.5	109.1	100.1	113.9	121.2	110.5	6.9
Atrazine	6.25	111.6	110.9	103.3	116.1	127.6	113.9	8.0
Simazine	2.50	110.6	107.2	101.3	113.2	126.5	111.7	8.4
Beiden	1.88	107.6	105.2	98.9	113.7	124.7	110.0	8.7
Ronnel	1.88	95.4	96.0	89.7	100.2	113.6	99.0	8.0
Alachlor	5.00	110.8	107.9	100.2	109.9	124.2	110.6	7.7
Ametryne	4.38	110.5	102.0	97.4	106.1	120.6	107.3	7.9
Sencor	5.00	112.2	107.5	100.1	111.3	119.9	110.2	6.4
Dursban	3.13	90.8	90.4	82.0	91.6	103.1	91.6	6.7
Malathion	1.88	110.3	105.9	103.0	109.8	129.3	111.7	9.2
Parathion	0.38	109.0	103.6	98.3	106.8	127.0	108.9	9.7
Bladex	3.75	110.6	92.5	87.9	94.6	118.7	100.9	11.7
Methyl Trithion	11.25	87.4	73.4	75.3	75.7	96.9	81.7	9.0
Ethion	3.75	71.3	67.5	68.9	69.4	88.5	73.1	7.8

The parameters investigated during the course of this work led to the development of the following method for the SPE of triazines and organophosphorous compounds.

Recommended Method for the SPE of Triazines and Organophosphorous Compounds

1. Determine the pH of the sample. If less than 7, increase the pH to 7 using 1 N potassium hydroxide solution.
2. Condition 500 mg C-18 columns by passing an aliquot of methanol (5 mL), followed by distilled water (5 mL) at a moderate flow rate. Do not allowed the columns to dry out.
3. Pass the sample (800 ml) through the column with vacuum assistance. Remove the vacuum from the apparatus following passage of the sample to prevent evaporative losses due to excessive air passage.
4. Centrifuge the columns briefly to remove excess water.
5. Slowly elute the analytes with 3 mL of ethyl acetate.
6. Quantitate using a gas chromatograph equipped with dual capillaries and thermionic specific detectors.

Conclusions:

Solid phase extraction allows the simultaneous determination of organophosphorous compounds and triazines in drinking waters. The method has consistent and high recoveries and low standard deviations, is rapid and easy to perform, and adsorbed triazines are stable for up to three months.



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